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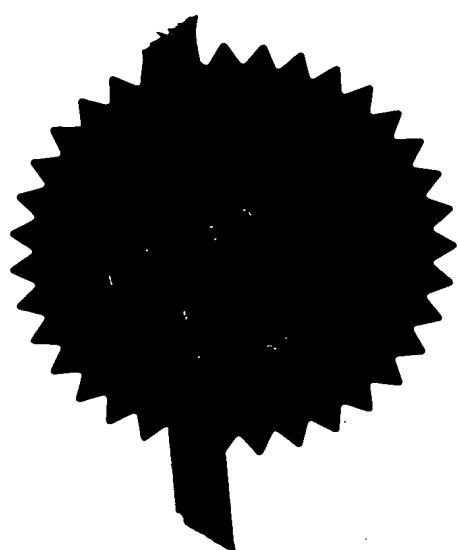
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4. Title of the invention

OXIDATION PROCESS

5. Name of your agent *(if you have one)*

DR NICHOLAS J WHITE

See AIC 26/6/98

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Abstract 1

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The present invention relates to an oxidation process and in particular to a process for the oxidation of unsaturated hydrocarbons in the presence of catalyst under heterogeneous conditions.

It is well known that the epoxidation of unsaturated hydrocarbons e.g. olefinic compounds, with various oxidants such as hydrogen peroxide may be effectively catalyzed by certain synthetic zeolites containing metal atoms such as titanium atoms (see, for example, U.S. Pat. No. 4,833,260).

Various process modifications have been proposed to improve the conversion and selectivity of these oxidation reactions. U.S. Pat. No. 4,824,976 proposes that the non-selective ring-opening reactions which take place when epoxidation is performed in a protic medium such as water or alcohol may be suppressed by treating the catalyst prior to the reaction or during the reaction with a suitable acid neutralising agent. The neutralising agent is said to neutralise acid groups on the catalyst surface which tend to promote by-product formation

U.S. Pat. No. 5,675,026 proposes the addition of neutral- or acid-reactive salts to the catalyst before or during the reaction to improve catalyst activity. U.S. Pat. No. 4,483,996 discloses a process for the conversion of olefins to olefin oxides and ketones. The process utilises a thalious catalyst, with molecular oxygen as

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oxidant in an aqueous carbon dioxide solvent. U.S. Pat. No. 5,591,875 proposes an epoxidation process which utilises a chelating agent to reduce the catalysts tendency to non-selectively decompose the hydrogen peroxide oxidant used. EP 0 385 631 A1 describes an oxidation process for the conversion of olefins to glycols utilising oxygen and carbon dioxide as reactants under supercritical conditions. A heterogeneous copper containing catalyst is proposed. U.S. Pat. No. 5,646,314 proposes performing the oxidation reaction in the presence of nonbasic salts in order to improve selectivity.

Furthermore it has long been recognised that metal containing zeolite catalysts rapidly become deactivated in use. There have been a number of methods developed to counter this deactivation and/or to regenerate the catalyst after use. U.S. Pat. No. 5, 741, 749 proposes a the regeneration of a titanium containing molecular sieve oxidation catalyst by treatment with a gas stream comprising specific amounts of molecular oxygen. WO 98/18555 proposes the regeneration of a titanium silicalite catalyst with a liquid solution of an oxidising agent. WO 98/ 18556 proposes the regeneration of a titanium silicalite catalyst under a specific gas flow

There are a number of problems with the processes of the prior art. Conversions and selectivities for the various reactions are in general still low or require additional process modifications which incur additional

costs. Frequently the catalyst systems utilised require special treatments and/or frequent regeneration in order to maintain catalyst activity.

5 It has been surprisingly found that the conversion and selectivity of oxidation processes, in particular the conversion of unsaturated hydrocarbons, especially olefins, to oxidation products especially oxirane compounds, are significantly improved by utilising a
10 specific group of catalysts in the presence of carbon dioxide. It has also been surprisingly found that the heterogeneous catalysts of the present process maintain their activity for significantly longer periods of time and through many recycles through the process. This
15 improved activity with respect to the catalyst means that costly and laborious pre-treatments and/or regenerations of the catalyst are either not required or are required at less frequent intervals in the process of the present invention compared to prior art processes.

20

Accordingly the present invention provides a process for the conversion of unsaturated hydrocarbons to one or more oxidation products which process comprises reacting one or more unsaturated hydrocarbons in a reaction
25 mixture under oxidation conditions in the presence of an oxidant, heterogeneous catalyst and a solvent characterised in that the catalyst comprises a Group IVB, VB or VIB metal and that carbon dioxide is present in the reaction mixture.

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In a preferred embodiment, the present invention

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pertains to an epoxidation process wherein a titanium containing catalyst is utilised in the presence of hydrogen peroxide as oxidant and the carbon dioxide is present in the reaction mixture under supercritical conditions.

Suitable oxidants for the process of the present

invention may be hydrogen peroxide or hydroperoxides. Examples of hydroperoxides include tert-butyl hydroperoxide (TBHP) and ethyl benzene hydroperoxide (EBHP). The preferred oxidant for the process of the present invention is hydrogen peroxide (H_2O_2). Hydrogen peroxide (H_2O_2) utilised as the oxidant in the present invention may be obtained from any suitable source, including, for example, from autoxidation of secondary alcohols using air or other source of molecular oxygen. Suitable secondary alcohols include both aliphatic alcohols such as isopropanol and cyclohexanol as well as aromatic alcohols such as alpha methyl benzyl alcohol and anthrahydroquinones (including alkyl-substituted anthrahydroquinones). The crude reaction product thereby generated may be either used directly in the epoxidation process of this invention or, if so desired, purified, fractionated, concentrated, ion exchanged, or otherwise processed prior to such use. For example, the ketone generated as an autoxidation co-product may be separated, in whole or in part, from the hydrogen peroxide by distillation (where the ketone is relatively volatile) or by extraction with water (where the ketone is substantially immiscible with or insoluble in water). The hydrogen peroxide may alternatively be generated in

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situ by, for example, combining oxygen, secondary alcohol, olefin, and catalyst within a reaction zone under conditions effective to accomplish simultaneous secondary alcohol autoxidation and olefin epoxidation.

5 Generally speaking, it will be desirable to employ initial hydrogen peroxide concentrations of from about 1 to 20 weight per cent in the liquid phase within the reaction zone.

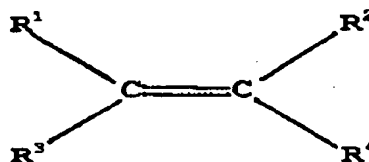
10 The unsaturated hydrocarbon is preferably an organic compound having from two to thirty carbon atoms and at least one ethylenically unsaturated functional group (i.e. a carbon-carbon double bond) and may be a cyclic, branched or straight chain aliphatic olefin. More than
15 one carbon-carbon double bond may be present in the olefin, dienes, trienes, and other polyunsaturated substrates thus may be used.

Exemplary olefins suitable for use in the process of
20 this invention include ethylene, propylene, the butenes, butadiene, the pentenes, isoprene, hexenes, heptenes, octenes, diisobutylene, nonenes, the trimers and tetramers of propylene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclooctadiene,
25 dicyclopentadiene, methylenecyclopropane, methylenecyclopentane, methylenecyclohexane, vinylcyclohexane, and vinyl cyclohexene.

Mixtures of olefins may be epoxidized and resulting
30 mixture of epoxides either employed in mixed form or separated into the different component epoxides.

The resulting epoxide or epoxide mixture may be rearranged to the corresponding linear aldehyde or ketone, either in-situ or in a separate step. Subsequent
5 oxidation or hydrogenation of the aldehyde or ketone will result in the corresponding linear acid or linear alcohol.

The process of this invention is especially useful
10 for the epoxidation of C₂-C₁₀ olefins having the general structure:



wherein R¹, R², R³, and R⁴ are the same or different and
15 are selected from the group consisting of hydrogen and C₁-C₈ alkyl (selected so that the total number of carbons in the olefin does not exceed 30).

The process of this invention is also suitable for
20 use in epoxidizing olefins containing functional groups other than aliphatic hydrocarbonyl moieties. For example, the carbon-carbon double bond can be substituted with groups such as -CO₂H, -CO₂R₁, -CN, or -OR wherein R is an alkyl, cycloalkyl, aryl or aralkyl substituent. The
25 radicals R¹, R², R³, and R⁴ in the structural formula

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shown hereinabove may contain aryl, aralkyl, halo, nitro, sulfonic, cyano, carbonyl, (e.g. ketone, aldehyde,) hydroxyl, carboxyl (e.g ester, acid) or ether groups. Examples of olefins of these types include allyl alcohol, styrene, allyl chloride, allyl methyl ether, allyl phenyl ether, methyl methacrylate, acrylic acid, methyl acrylate, stilbene, and the like.

The amount of hydrogen peroxide relative to the amount of olefin is not critical, but most suitably the molar ratio of olefin: hydrogen peroxide is from about 100:1 to 1:10 when the olefin contains one ethylenically unsaturated group. The molar ratio of ethylenically unsaturated groups in the olefin to hydrogen peroxide is more preferably in the range of from 1:2 to 10:1.

The heterogeneous catalysts contain a Group IVB, VB or VIB metal and may be crystalline and/or amorphous. The most preferred catalysts contain a Group IVB metal. Particularly preferred catalysts are crystalline molecular sieves especially zeolites which contain titanium.

The titanium silicalites useful as catalysts in the epoxidation step of the process comprise the class of zeolite substances wherein titanium is substituted for a portion of the silicon atoms in the lattice framework of a molecular sieve. Such substances are well-known in the art.

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Particularly preferred titanium silicalites include

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the classes of molecular sieves commonly referred to as "TS-1" (having an MFI topology analogous to that of the ZSM-5 aluminosilicate zeolites), "TS-2" (having an MEL topology analogous to that of the ZSM-11 aluminosilicatezeolites), and "TS-3" (as described in Belgian Pat. No. 1,001,038). Also suitable for use are the titanium-containing molecular sieves having framework structures isomorphous to zeolite beta. Also suitable is TS-48 with the structure of zeolite ZSM-48 as well as titanium mordenite with the MOR structure. The titanium silicalite preferably contains no non-oxygen elements other than titanium and silica in the lattice framework, although minor amounts of boron, iron, aluminum, and the like may be present.

15

Titanium silicalite catalysts suitable for use in the process of this invention will generally have a composition corresponding to the following empirical formula $x\text{TiO}_2:(1-x)\text{SiO}_2$, where x is between 0.0001 and 0.500. More preferably, the value of x is from 0.01 to 0.125. The molar ratio of Si:Ti in the lattice framework of the titanium silicalite is advantageously from 9.5:1 to 99:1 (most preferably, from 9.5:1 to 60:1). The use of relatively titanium-rich silicalites may also be desirable. The preferred catalyst is titanium silicalite-1. One form of catalyst suitable for use in the process of the present invention is a "cherry type" catalyst which consists of a core of material e.g. silica/alumina and a shell of different material e.g. silica/titania as described for example in EP 634 212.

30

The amount of catalyst employed is not critical, but should be sufficient so as to substantially accomplish the desired epoxidation reaction in a particularly short period of time. The optimum quantity of catalyst will depend upon a number of factors including reaction temperature, olefin reactivity and concentration, hydrogen peroxide concentration, type and concentration

of organic solvent as well as catalyst activity and the type of reactor or reaction system (i.e. batch vs continuous) employed. In a batch-type or slurry reaction, for example, the amount of catalyst will typically be from 0.001 to 10 grams per mole of olefin. In a fixed or packed bed system, the optimum quantity of catalyst will be influenced by the flow rate of reactants through the fixed bed; typically, from about 0.05 to 2.0 kilograms hydrogen peroxide per kilogram catalyst per hour will be utilised. The concentration of titanium in the liquid phase reaction mixture will generally be from about 10 to 10,000 ppm.

The catalyst may be utilised in powder, pellet, microspheric, extruded, monolithic or any other suitable physical form. The use of a binder (co-gel) or support in combination with the titanium silicalite may be advantageous. Supported or bound catalysts may be prepared by the methods known in the art to be effective for zeolite catalysts in general. Preferably, the binder or support is essentially non-acidic and does not catalyze the non-selective decomposition of hydrogen peroxide or ring-opening of the epoxide.

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Illustrative binders and supports include titania, silica, alumina, silica-alumina, silica-titania, silica-thoria, silica-magnesia, silica-zirconia, silica-beryllia, and ternary compositions of silica with other refractory oxides. Also useful are clays such as montmorillonites, koalins, bentonites, halloysites, dickites, nacrites, and anaxites. The proportion of titanium silicalite binder or support may range from 99:1 to 1:99, but preferably is from 5:95 to 80:20.

10 The epoxidation reaction temperature is preferably from 0°C to 100°C (more preferably from 40°C to 80°C), which has been found to be sufficient to accomplish selective conversion of the olefin to epoxide within a reasonably short period of time with minimal non-
15 selective decomposition of the hydrogen peroxide. It is generally advantageous to carry out the reaction to achieve as high a hydrogen peroxide conversion as possible, preferably at least 50%, more preferably at least 90%, most preferably at least 99%, consistent with
20 high selectivities. The optimum reaction temperature will be influenced by catalyst concentration and activity, substrate reactivity, reactant concentrations and type of solvent employed, among other factors. Reaction or residence times of from about 10 minutes to
25 48 hours will typically be appropriate, depending upon the above-identified variables. The reaction is preferably performed at atmospheric pressure or at elevated pressure (typically, between 1 and 700 atmospheres). Generally, it will be desirable to
30 maintain the reaction components as a liquid mixture. For example, when an olefin such as propylene is used

having a boiling point at atmospheric pressure which is less than the epoxidation temperature, a superatmospheric pressure sufficient to maintain the desired concentration of propylene in the liquid phase is preferably utilised.

5 The epoxidation process of this invention may be carried out in a batch, continuous, or semi-continuous manner using any appropriate type of reaction vessel or apparatus such as a fixed bed, transport bed, stirred slurry, or CSTR reactor. Known methods of conducting metal-catalysed epoxidations using hydrogen peroxide will
10 generally also be suitable for use. Thus, the reactants may be combined all at once or sequentially. For example, the hydrogen peroxide and/or the olefin may be added incrementally to the reaction zone.

15 The oxidation must be carried out in the presence of carbon dioxide in the gaseous, liquid or supercritical state. It is most preferred that the carbon dioxide is present in the supercritical state which is where it exists as a one phase fluid occurring above both a
20 critical temperature and pressure T_c and P_c , which is 31°C and 73.8 kg/cm^2 . The reaction mixture including catalyst comprises at least 1% by weight of carbon dioxide, preferably at least 10% by weight and more preferably at least 25% by weight of the reaction mixture
25 including catalyst. In a most preferred embodiment the carbon dioxide constitutes more than 50% by weight of the solvent used in the reaction mixture.

Any solvent or combination of solvents which are compatible with carbon dioxide may be used. The

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preferred solvent has methanol as its main constituent in combination with carbon dioxide. Other suitable solvents include, but are not limited to water alcohols (especially C₁-C₁₀ aliphatic alcohols such as methanol and isopropanol); ketones (especially C₃-C₁₀ ketones such as acetone), and mixtures of such solvents. It is preferred that supercritical carbon dioxide is present as the solvent or in admixture with other solvents. Accordingly carbon dioxide when present as a solvent should be at least 1% by weight of the solvent mixture and preferably at least 5 to 100%, most preferably 25 to 100% by weight of the solvent. In a most preferred embodiment the carbon dioxide comprises at least 50% by weight of the solvent.

Once the epoxidation has been carried out to the desired degree of conversion, the epoxide product may be separated and recovered from the reaction mixture using any appropriate technique such as fractional distillation, extractive distillation, liquid-liquid extraction, crystallisation, or the like. After separating from the epoxidation reaction mixture by any suitable method such as filtration (as when a slurry reactor is utilised, for example), the recovered titanium silicalite catalyst may be economically re-used in subsequent epoxidations. Where the catalyst is deployed in the form of a fixed bed, the epoxidation product withdrawn as a stream from the epoxidation zone will be essentially catalyst free with the catalyst being retained within the epoxidation zone. Similarly, any unreacted olefin or hydrogen peroxide may be separated and recycled or otherwise disposed of. In certain embodiments of the instant process where the epoxide is

produced on a continuous basis, it may be desirable to periodically or constantly regenerate all or a portion of the used catalyst in order to maintain optimum activity and selectivity. Suitable regeneration techniques are well-known and include, for example, calcination and solvent treatment. Such regeneration and/or treatment may not be necessary until a significant number of recycles have occurred through the process of the present invention.

From the foregoing description, one skilled in the art can readily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof can make various changes and modifications of the invention to adapt it to various usages, conditions, and embodiments.

The present invention is further illustrated by means of the following examples:

Example 1

A TS-1 catalyst (prepared by the procedure given in Applied Catalysis, 99, (1993), pages 71-84) was utilised in the oxidation of 1-octene to 1,2-epoxyoctane with and without supercritical carbon dioxide as the solvent. A 250 cm³ batch autoclave equipped with a temperature controller, mechanical stirrer, reagents feed line, sampling line and vent line was charged in two separate experiments with the following reagents.

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Reagents	Experiment 1	Experiment 2
	Weight (g)	Weight (g)
1-octene	14.52	7.26
H ₂ O ₂ (30wt% in H ₂ O)	0.44	0.22
Methanol	112.5	56.25
Carbon Dioxide	0	74.2
TS-1 catalyst	1.0	0.5
Total	128.46	138.43

For Experiment 1 the reaction was undertaken at 65°C for 60 minutes. For Experiment 2 the reactor was first pressurised with carbon dioxide gas to 48 bar (48×10^5 5 Nm^{-2}), after which 74.2g of liquid carbon dioxide was added. The reaction was undertaken at 65°C for 60 minutes and at a pressure of 106 bar ($106 \times 10^5 \text{Nm}^{-2}$). The composition of the reaction mixtures was determined using Gas Chromatography and the hydrogen peroxide 10 content was determined using iodometric titration.

The results are provided in Table 1.

Table 1			
Experiment	Mole % 1,2-epoxyoctane	Mole % Glycolethers	% Conversion of H ₂ O ₂
1	77.8	22.2	97.9
2	91.1	8.9	98

It can be seen from the above results that for a given conversion the selectivity is greatly enhanced when carbon dioxide is used in the oxidation utilising TS-1 as catalyst.

Example 2

In a further set of experiments the solvent system utilised was methanol or methanol/CO₂ under supercritical conditions.

10 In a first set of experiments (Experiment 3) the TS-1 catalyst was used in a methanol solvent and recycled without treatment or regeneration. In a second set of experiments (Experiment 4) the TS-1 catalyst was used in a methanol/carbon dioxide solvent system under
15 supercritical conditions with respect to the carbon dioxide again the catalyst was recycled without further treatment or regeneration.

Methanol Solvent - Catalyst Recycle

The following reagents were used:

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Reagents	Experiment 3
	Weight (g)
1-octene	7.26
H ₂ O ₂ (30wt% in H ₂ O)	0.22
Methanol	56.3
Carbon Dioxide	0
TS-1 catalyst	0.5
Total	64.23

The reaction was undertaken at 40°C for 60 minutes in a 100 cm³ glass reactor with magnetic stirrer and chilled water cooler on an electrical heating mantle. On completion the reactor was recharged with reagents and the used catalyst was recycled by filtration and drying in vacuo at room temperature for 10 minutes. The catalyst was recycled twice and the results are provided in Table 2.

Table 2			
Run Number	Mole % 1,2-epoxyoctane	Mole % Glycolethers	%Conversion of H ₂ O ₂
1.Fresh catalyst	89.5	10.5	90.1
2.First recycle	100	0	52.0
3.Second recycle	100	0	28.4

It can be seen from the results in Table 2 that the conversion of hydrogen peroxide is dramatically reduced on recycling the catalyst.

Methanol Solvent with Carbon Dioxide - Catalyst Recycle

5 The following reagents were used:

Reagents	Experiment 3
	Weight (g)
1-octene	7.26
H2O2 (30wt% in H2O)	0.22
Methanol	56.25
Carbon Dioxide	82.8
TS-1 catalyst	0.5
Total	147.03

10 A 250 cm³ batch autoclave equipped with a temperature controller, mechanical stirrer, reagents feed line, sampling line and vent line was filled with all the above reagents except carbon dioxide and 1-octene. Then the reactor was pressurised with carbon dioxide gas to 52 bar (52 x 10⁵ Nm⁻²), after which 82.6g of liquid carbon dioxide was added, then 1-octene was injected and the
15 reaction was undertaken at 40°C for 30 minutes and at a pressure of 74.3 bar (74.3 x 10⁵ Nm⁻²). On completion of

the reaction the catalyst was removed by filtration and dried in air before being twice recycled using the same reactor, reagents and conditions. The results are provided in Table 3.

5

Table 3			
Run Number	Mole % 1,2-epoxyoctane	Mole % Glycolethers	%Conversion of H2O2
1.Fresh catalyst	100	0	96
2.First recycle	100	0	96
3.Second recycle	100	0	88

10

It can be seen from the results in Table 3 that utilising carbon dioxide in the reaction enables the catalyst to be recycled without a dramatic reduction in hydrogen peroxide conversion whilst maintaining a high selectivity towards the desired epoxide.

Claims

1. A process for the conversion of unsaturated hydrocarbons to one or more oxidation products which
5 process comprises reacting one or more unsaturated hydrocarbons in a reaction mixture under oxidation

conditions in the presence of an oxidant, heterogeneous catalyst and a solvent characterised in that the catalyst comprises a Group IVB, VB or VIB metal and that carbon
10 dioxide is present in the reaction mixture.

2. A process as claimed in claim 1 wherein the catalyst is a metal molecular sieve.

15 3. A process as claimed in claim 1 or claim 2 wherein the metal is a Group IVB metal.

4. A process as claimed in claim 3 wherein the metal is titanium.

20 5 A process as claimed in any one of claims 1 to 4 wherein the solvent is methanol.

6. A process as claimed in any of the preceding claims
25 wherein the oxidant is hydrogen peroxide.

7. A process as claimed in any one of the preceding claims wherein the unsaturated hydrocarbon is an olefin.

30 8. A process as claimed in any an of the preceding claims wherein the oxidation product is an epoxide, aldehyde, ketone or acid.

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ABSTRACT**Oxidation Process**

The selectivity of an olefin epoxidation process
5 catalyzed by a heterogeneous catalyst for example
titanium silicalite is improved by performing the
epoxidation in the presence of carbon dioxide. The
catalysts used do not require regeneration on each
recycle.

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